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Thermal Ionization and Electronegative Species

21 SEPTEMBER 1962

*Prepared by A. E. FUHS
Physical Research Laboratory*

Prepared for COMMANDER BALLISTIC SYSTEMS DIVISION

UNITED STATES AIR FORCE

Inglewood, California



LABORATORIES DIVISION • AEROSPACE CORPORATION

CONTRACT NO. AF 04(695)-169

BSD-TDR-62-238

Report No.
TDR-169(3153)TN-2

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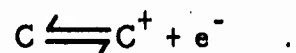
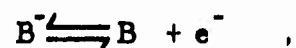
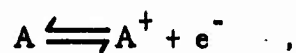
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ABSTRACT

Free electrons that are present in the ionized gas of the re-entry plasma sheath or the exhaust of rockets cause severe attenuation and reflection of electromagnetic waves. A frequently proposed solution to the resultant communication problem is the addition of trace amounts of an electronegative species.

The aim of the study described in this paper is to examine the conditions which are favorable or unfavorable for "soaking up" electrons. The work of Sanochkin is extended to include thermal ionization in gas mixture with electronegative species. General formulas are specialized for the reactions



A model gas is used where each species is characterized by its ionization potential or its electron affinity. The degree of ionization (i. e., ratio of electron to particle density), the fraction of A, B, or C ionized, and the ratio of electron density with and without additives have been calculated as a function of kT with pressure and mole fraction of additives as parameters. The notation (I_A, I_B, I_C) was used to identify a mixture, where I_A is ionization potential in electron volts of species A, etc.; calculations were performed for (4, 4, ∞), (16, 4, ∞), (16, 4, 4), (4, 2, ∞), (16, 2, 4), and (16, 4, 2) mixtures.

When ionization potential and electron affinity are equal, electrons are absorbed efficiently up to kT of about $I/10$. When ionization potential exceeds the electron affinity, the efficiency for free electron removal decreases markedly. If $I_A \leq I_B$, calculations show that a mixture of equal parts of A and B would be an all-ion (nearly) plasma at low energy.

An experiment was conducted in which the conductivity of an argon plasma jet and the conductivity of an argon-with-SF₆ plasma jet were measured. The results of the experiment are consistent with the calculations.

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SECTION I

INTRODUCTION

One approach to the solution of the problem of communications blackout during re-entry is to decrease the electron density. Rosen¹ proposes injection of a ceramic dust as a means of absorbing electrons. Another method considered² is injection of an electronegative species. The negative ions which are formed have far less influence on electromagnetic waves at telemetry frequencies than do electrons.

Another area where communication difficulties are experienced due to the presence of ionized gases is the boost phase of launch. A trace amount of an impurity which is added to the propellant and which has a strong electron affinity might cause a significant reduction in electron density.

This note extends the work of Sanochkin³ to include gas mixtures with electronegative species under conditions of thermodynamic equilibrium. After the general formulas have been derived, several special cases are examined.

SECTION II

FORMULATION FOR GAS MIXTURES

A. Definition of Symbols

The following symbols are used:

N_{kj} = number per unit volume of molecules of species j
with charge k

$N_j = \sum_k N_{kj}$ = number density of molecules of species j

$N = \sum_j N_j$ = number density of all molecules (note that
number density of electrons is not included)

N_e = number density of electrons

$X_j = N_j/N$ ($\sum X_j = 1$) number fraction of species j

A series of additional symbols is useful for comparing the number of ions and electrons to the number of molecules present; these are:

$a_{kj} = N_{kj}/N_j$ = fraction of species j with charge k

$a_j = \sum_k k N_{kj}/N_j = \sum_k k a_{kj}$ = average charge considering all
molecules of species j

$\alpha = N_e/N = \sum_j a_j$ = apparent degree of ionization of gas
mixture

An alternate interpretation of a_j is that it is the average number of electrons due to species j as compared with the number of species j molecules. Also, α can be thought of as the number of electrons relative to the total number of all molecules.

The index k can be negative as well as positive. For the reactions considered in this note, k runs from $-l$ to Z , where l is the number of charges on a negative ion and Z is the atomic number of the particular species. The reactions are identified by k as follows:

| <u>Reaction</u> | <u>Identification in Terms of k</u> |
|------------------------------------|--|
| $A^- \rightarrow A + e^-$ | -1 |
| $A \rightarrow A^+ + e^-$ | 0 |
| $A^+ \rightarrow A^{++} + e^-$ | 1 |
| $A^{++} \rightarrow A^{+++} + e^-$ | 2 |
| | |

B. Equilibrium Constants

The equilibrium constant for the ionization reaction is

$$K_j^{(k+1)} = \frac{p_{k+1,j} p_e}{p_{kj}}$$

where p_{kj} is partial pressure of species j with charge k and p_e is partial pressures of electrons. Perfect gases are assumed so that $p_{kj} = N_{kj} kT$. Equation (1) is discussed extensively in Penner⁴ and Landau and Lifshitz.⁵ Equation (1) can be rewritten as

$$\frac{K_j^{(k+1)}}{p} = \frac{p_{k+1,j} p_e}{p_{kj} p} = \frac{N_{k+1,j} N_e}{N_{kj} (N + N_e)} = \frac{N_{k+1,j}/N_j}{N_{kj}/N_j} \frac{N_e/N}{1 + N_e/N}$$

The result is

$$\frac{a_{k+1,j}}{a_{kj}} = \frac{1 + a}{a} \frac{K_j^{(k+1)}}{p}$$

where p is total pressure of gas mixture.

The equilibrium constant is obtained from

$$K_j^{(k+1)} = \frac{2Q_{k+1,j}}{Q_{kj}} \left(\frac{2\pi m_e}{h^2} \right)^{3/2} (kT)^{5/2} \exp - \frac{I_{k+1,j}}{kT} \quad (4)$$

where Q_{kj} is the partition function for the k -ion of species j and m_e is the mass of an electron. Equation (4) is well known and is derived in Ref. 5. Numerical values of the equilibrium constant are tabulated in Appendix A.

C. Solution for Degree of Ionization of Species j

Use is made of the fact that summation over k of a_{kj} gives unity. As stated previously, k runs from $-l$ to Z . The solution for a_{mj} is built up as follows:

$$a_{mj} = \frac{a_{mj}}{\sum_{k=-l}^Z a_{kj}} = \frac{a_{mj}/a_{-lj}}{\sum_{k=-l}^Z a_{kj}/a_{-lj}} \quad (5)$$

The ratio a_{mj}/a_{-lj} and similar ratios in the denominator are

$$\frac{a_{mj}}{a_{-lj}} = \frac{a_{mj}}{a_{m-1,j}} \frac{a_{m-1,j}}{a_{m-2,j}} \dots \frac{a_{1-l,j}}{a_{-l,j}} \quad (6)$$

and

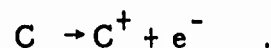
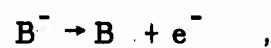
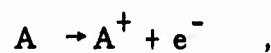
$$\frac{a_{mj}}{a_{-lj}} = \left(\frac{1+a}{a} \right)^{m+l} \frac{\prod_{r=1-l}^m K_j^{(r)}}{p^{m+l}} \quad (7)$$

Equations (5) and (7) are combined to yield

$$a_{mj} = \frac{\left(\frac{1+a}{a}\right)^{m+l} p^{-(m+l)} \prod_{r=1-l}^m K_j^{(r)}}{1 + \sum_{k=1-l}^Z \left(\frac{1+a}{a}\right)^{k+l} p^{-(k+l)} \prod_{r=1-l}^k K_j^{(r)}} \quad (8)$$

D. Models for Different Species

Equation (8) will be specialized for two-species and three-species gas mixtures which have the reactions



The molecules A, B, and C are characterized solely by ionization potential or electron affinity. The ratio of partition functions has been set equal to unity.

SECTION III

TWO-SPECIES GAS MIXTURES

This section is a discussion of mixtures of molecules A and B. From Eq. (8) the fraction of A molecules that are ionized is

$$a_{1A} = \frac{[(1 + a)/a] (K_A/p)}{1 + [(1 + a)/a] (K_A/p)} \quad (9)$$

In Eq. (9), the superscript on the equilibrium constant has been omitted. The value for the fraction of neutral molecules is $1 - a_{1A}$. Likewise, from Eq. (8), the fraction of B molecules which are negative ions is found to be

$$a_{-1B} = \frac{1}{1 + [(1 + a)/a] (K_A/p)} \quad (10)$$

Using the definition for a_j , one finds that $a_B = -a_{-1B}$ and that $a_A = a_{1A}$. The summation of $X_j a_j$ gives a which, for this case, is

$$a = X_A a_{1A} - X_B a_{-1B} \quad (11a)$$

or,

$$a = X_A a_{1A} - X_B (1 - a_{0B}) \quad (11b)$$

Combination of Eqs. (9), (10), and (11) provides an expression for a :

$$\frac{a}{1 + a} = \frac{X_A}{1 + a \left[1 + (p/K_A) \right]} + \frac{X_B}{1 + a \left[1 + (p/K_B) \right]} - \frac{X_B}{1 + a} \quad (12)$$

The degree of ionization of a pure species α^* can be obtained from Eq. (12) by setting $X_A = 1$ and $X_B = 0$. The result is

$$\alpha^* = \left(1 + \frac{p}{K_A}\right)^{-1/2} \quad (13)$$

Equation (12) has been solved for α as a function of kT with pressure p as a parameter. In the calculation of the equilibrium constant, the ratio of partition functions has been set equal to unity. Addition of an electronegative species B will change α . The influence depends on the ratio of equilibrium constants:

$$\frac{K_A}{K_B} = \exp - \frac{I_A - I_B}{kT} \quad (14)$$

Three cases have been considered; the energy diagrams are illustrated in Fig. 1. The results of the calculation will now be discussed.

A. Addition of a Trace Amount to a Pure Component

1. Condition When K_A/K_B Is Much Less Than Unity

The ionization potential for species A exceeds the electron affinity of species B . Numeral values chosen were $I_A = 16$ and $I_B = 4$. Different amounts of electronegative species were added, namely, $X_B = 0.1, 0.01, \text{ and } 0.001$. The pressure was 10^3 newtons/m² or about 0.01 atmosphere. The results are shown graphically in Fig. 2. If the electronegative species is to "soak up" the electrons, nearly every molecule of B should be a negative ion. A measure of the amount* of B^- is α_{1B} . Note that α_{1B} never exceeds 2×10^{-5} ; hence, only two out of 100,000 B molecules ever unite with an electron. There is a maximum in the curve of α_{1B} at about 1 ev. Below that, energy A is not sufficiently

*The symbol α_{1B} replaces α_{-1B} for the remainder of the report.

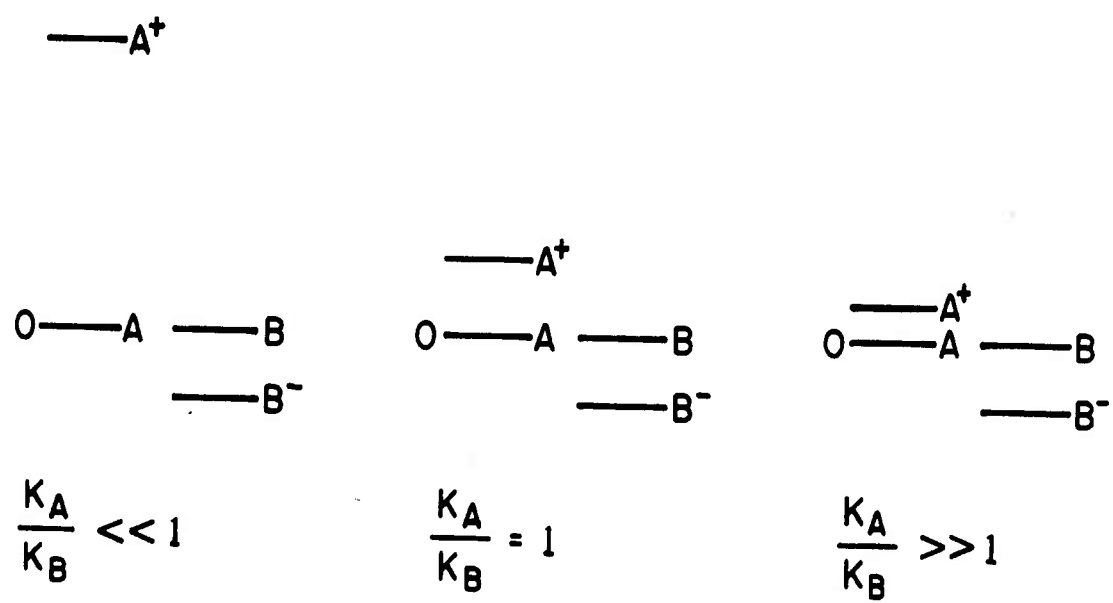


Fig. 1. Energy level diagrams for three values for the ratio of equilibrium constants.

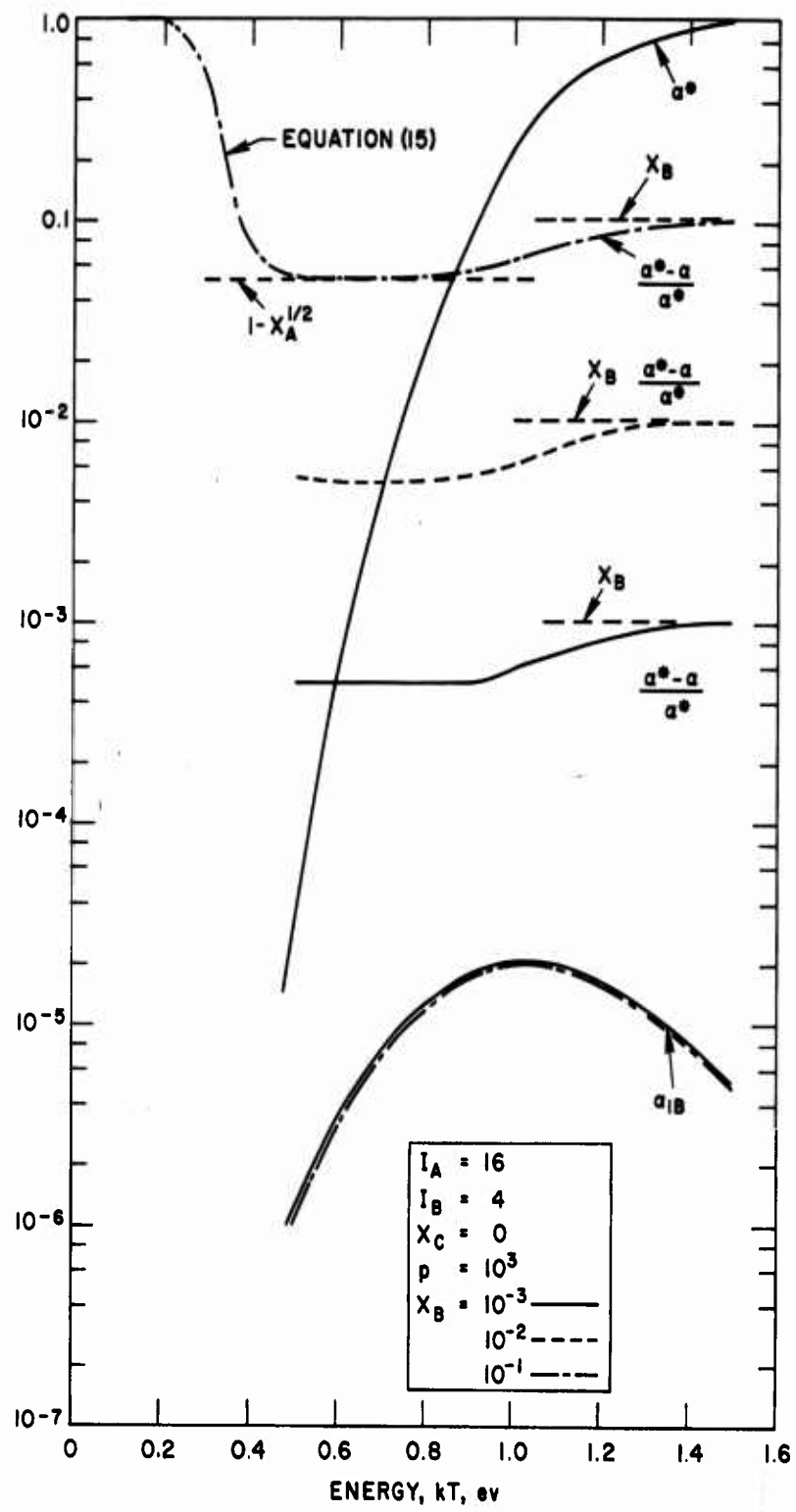


Fig. 2. Graphs of ionization for $I_A = 16$ and $I_B = 4$.

ionized to provide electrons to form B^- . In other words, if there is to be a B^- there must be an A^+ ion, and there are few A^+ ions below 1 ev. Above 1 ev there is sufficient energy available to depopulate the B^- state.

Another measure of the efficiency of the electronegative species is $(a^* - a)/a^*$, the fractional decrease in the number of electrons. At low energy this quantity approaches unity, which means nearly all electrons are captured by B molecules; however, at low energies N_e is very small and of no concern. From about 0.4 ev to 0.8 ev, $(a^* - a)/a^*$ approaches $1 - X_A^{1/2}$. For trace amounts of B, $1 - X_A^{1/2}$ is approximately $X_B/2$. At higher energies, X_B is approached as A becomes fully ionized, and B exists as neutrals.

For energy up to 0.5 ev, a is given approximately by

$$a = 1 - \left(\frac{X_A}{1 + X_B p/K_B} \right)^{1/2} \quad (15)$$

Calculations were also performed for $I_A = 4$ and $I_B = 2$. The results are shown in Fig. 3. Once again a_{1B} attains a maximum value. At low degrees of ionization, for conditions stated in Fig. 3, the number of electrons is reduced as the following table shows.

| $kT, \text{ ev}$ | $N_e, \text{ cm}^{-3}$ | $N_e^*, \text{ cm}^{-3}$ |
|------------------|------------------------|--------------------------|
| 0.10 | 9.5×10^7 | 1.7×10^{10} |
| 0.12 | 1.9×10^{10} | 5.0×10^{11} |
| 0.14 | 8.3×10^{11} | 5.6×10^{12} |
| 0.20 | 4.0×10^{14} | 4.5×10^{14} |

As temperature increases the electrons are not absorbed by the electronegative species.

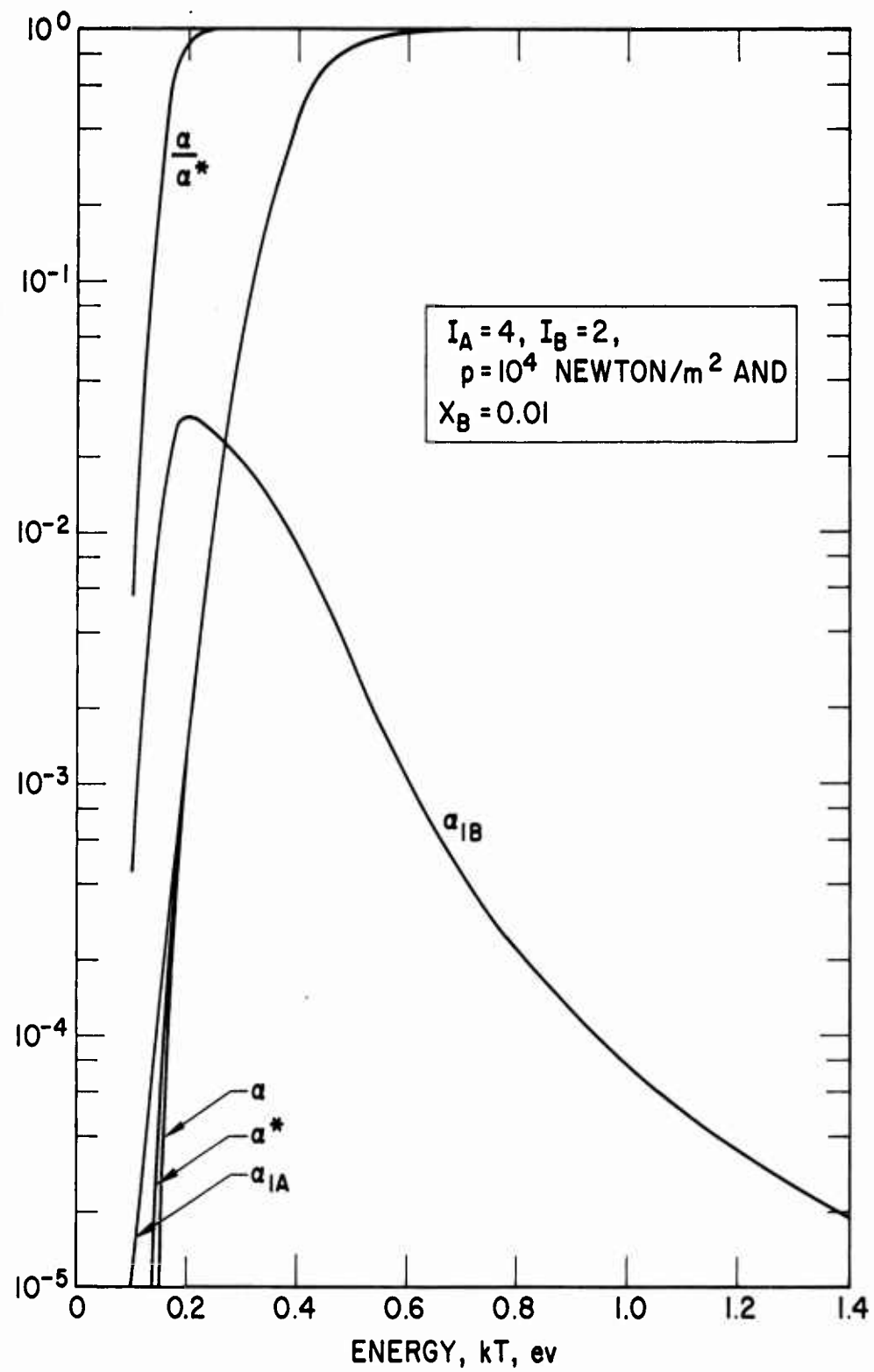


Fig. 3. Graphs of ionization for $I_A = 4$ and $I_B = 2$.

2. Condition When K_A/K_B Equals Unity

For this special case, Eq. (12) can be solved explicitly for α ; the solution is

$$\alpha = \frac{X_B}{2} \left[\sqrt{1 + \frac{4X_A}{X_B^2 (1 + p/K)}} - 1 \right] \quad (16)$$

When the energy of gas is low, the square root can be expanded giving an approximate formula for α :

$$\alpha \approx \frac{X_A}{X_B} \frac{K}{p} \quad (17)$$

Combining Eq. (17) with Eqs. (9) and (10), one finds that $\alpha_{1A} \rightarrow X_B$ and $\alpha_{1B} \rightarrow X_A$ at low energy. For low energy, α^* is approximately $(K/p)^{1/2}$. The fractional decrease in electron density α/α^* is approximately

$$\frac{\alpha}{\alpha^*} = \frac{X_A}{X_B} \left(\frac{K}{p} \right)^{1/2} \quad (18)$$

At high energy, $\alpha_{1A} \rightarrow 1$, $\alpha_{1B} \rightarrow 0$, $\alpha \rightarrow X_A$, and $\alpha/\alpha^* \rightarrow X_A$.

Figure 4 has linear plots of the various α for $I_A = I_B = 4$, $X_B = 0.1$, and $p = 10^3$ newton/m². Figure 5 has the same values for I_A , I_B , X_B , and p , but it is a semilogarithmic plot.

Up to about 0.3 ev, nearly every B molecule is a negative ion which means that the electrons are effectively removed. Above 0.3 ev, B^- ions gradually become neutral B.

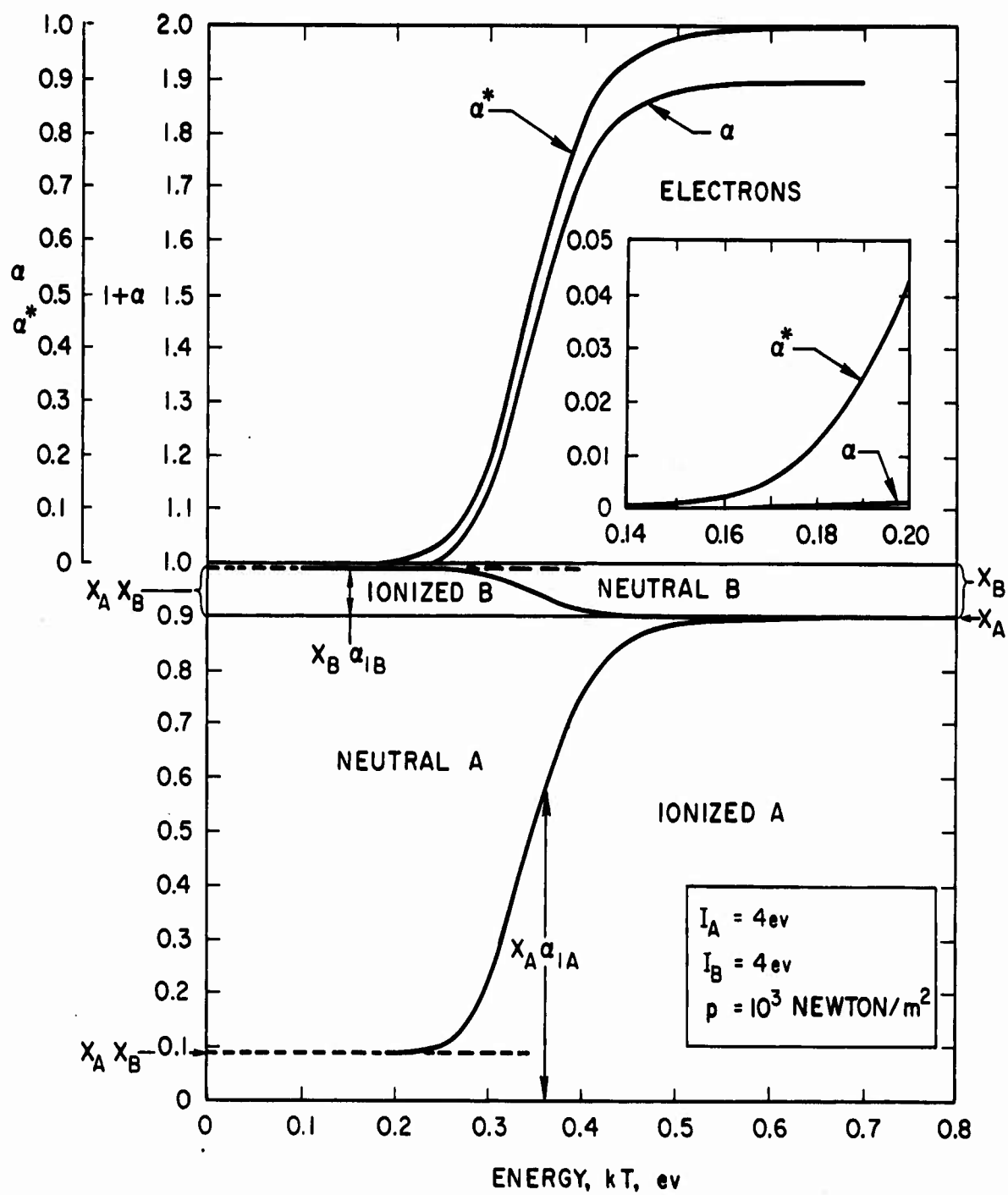


Fig. 4. Linear graphical representation of the degree of ionization of a (4, 4) gas mixture as a function of energy.

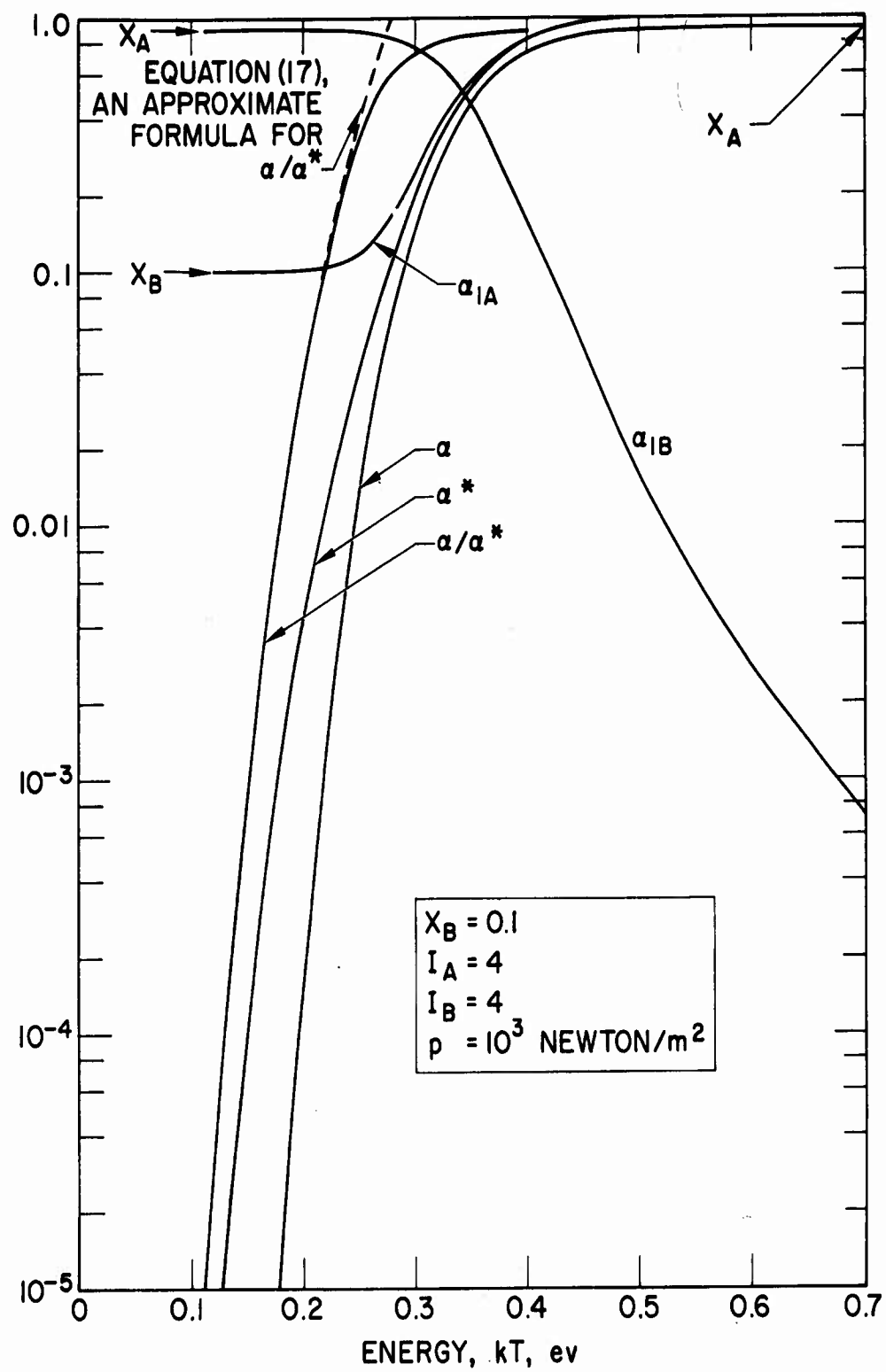


Fig. 5. Degree of ionization for a (4, 4) gas mixture as a function of energy.

The ratio of electron density with electronegative species to electron density of pure gas, which is α/α^* , increases from very small values at low energy to approach X_A at high energy. Hence, at low energy an electronegative species is very efficient in eliminating free electrons. At low energy, the gas mixture is mainly neutral A, with nearly equal numbers of A^+ and B^- and with very few electrons. The gas could be described as a neutral-all-ion mixture. At high energy, the gas mixture is composed of ion-electron plasma with a trace of neutral B. There are very few B^- .

Equation (18) begins to diverge from accurate calculation of α/α^* when α/α^* exceeds 0.1. Hence, an estimate of the influence of an electronegative species can be readily obtained from Eq. (18). Equation (18) also provides an indication of the influence of pressure. Increasing pressure shifts the α/α^* curve toward higher energy.

The high- and low-energy limits which were previously discussed in connection with Eqs. (16), (17), and (18) are indicated in Figs. 4 and 5.

When $I_A = I_B$, addition of electronegative species effectively reduces the electron density at low energy. For example, Fig. 5 shows that at $kT = 0.15$ ev, 999 out of 1000 electrons are removed.

3. Condition When $K_A/K_B \gg 1$

Calculations were performed for $I_A = 2$ and $I_B = 4$. Two different pressures were used, 10^4 and 10^6 newton/m². Figure 6a shows the results for $X_B = 0.01$; Fig. 6b shows the results for $X_A = X_B = 0.5$.

The fraction of A ionized, as seen in Fig. 6a, rises from X_B/X_A at low energy to unity at high temperature. The low-energy value for α_{1B} is unity. The number of B ionized decreases as temperature increases. The electronegative species B efficiently removes free electrons (as evidenced by low values of α/α^*) up to the "kink" in the α_{1A} curve at about $kT = 0.15$ ev.

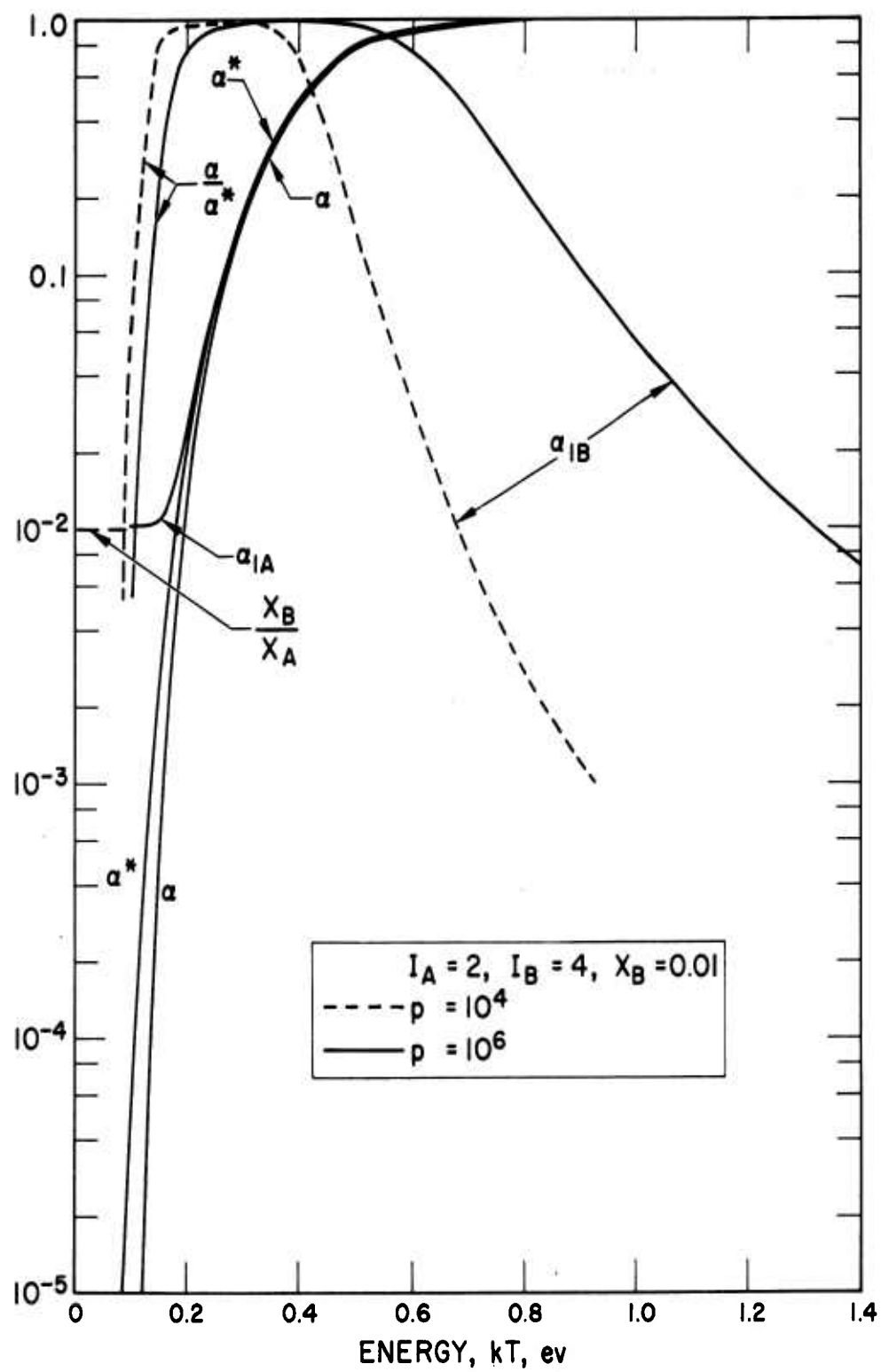


Fig. 6a. Degree of ionization for a (2, 4) mixture with a trace amount of electronegative species.

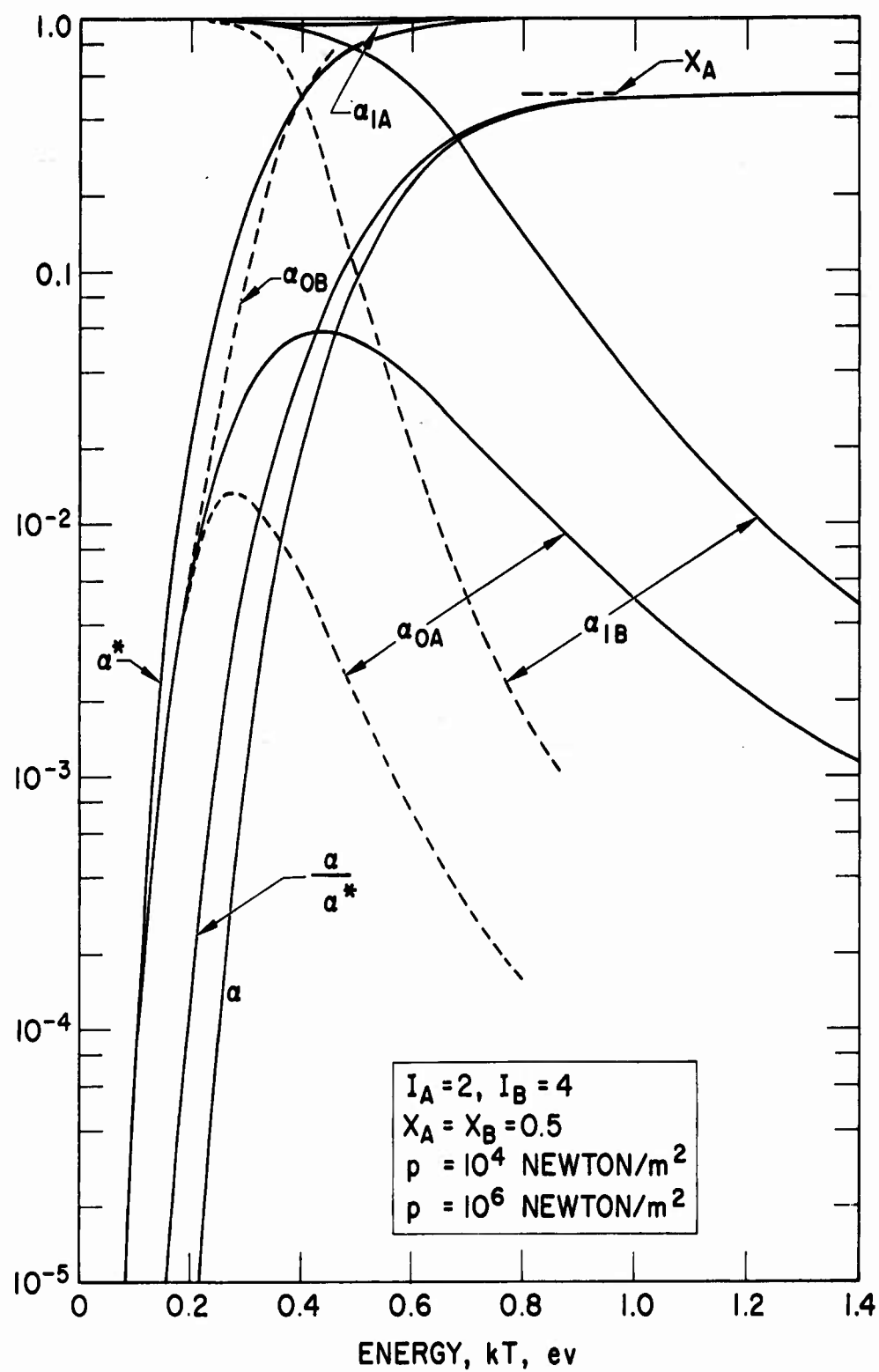


Fig. 6b. Degree of ionization for a (2, 4) mixture with equal parts of species A and B.

When $X_A = X_B$, the gas mixture is an all-ion plasma with very few neutrals. At $kT = 0.2$ ev, for $p = 10^4$, $\alpha_{1A} = 0.9936$ and $\alpha_{1B} = 0.9930$.

In the energy interval $0.2 < kT < 0.4$, α_{1A} decreases as the gas energy increases. The origin of this unusual trend is the fact that the combination B^- and A^+ has less energy by 2 ev than the combination B and A.

The question arises as to whether or not a gas mixture with the properties assumed here is physically realizable. It probably is not, because A and B would have a strong tendency to form a molecule AB. Figure 6b points out the fact that a cool all-ion plasma might be possible. A candidate for B could be SF_6 .

B. Low-Energy, All-Ion Plasma

The low-energy limits for the degree of ionization when the ionization potential and electron affinity are equal ($I_A = I_B$) suggests the formation of an all-ion plasma. Calculations were performed for a gas mixture composed of equal parts of A and B, using $I_A = I_B = 4$ ev and $p = 10^3$ and 10^4 newtons/m². The results are presented in Figs. 7 and 8. At low energies, as previously discussed, $\alpha_{1A} \rightarrow X_B$ and $\alpha_{1B} \rightarrow X_A$. For this case, where $X_A = X_B = 0.5$, the plasma is composed of nearly equal numbers of A^+ , A , B^- , and B, i. e., the plasma is one-fourth A , one-fourth A^+ , etc. There are very few electrons relative to the number of negative ions.

This statement is expressed quantitatively by

$$\frac{N_e}{N_{B^-}} = \frac{\alpha N}{\alpha_{1B} N_B} = \frac{\alpha}{\alpha_{1B} X_B} \quad (19)$$

The ratio is plotted in Fig. 7.

As pressure is decreased, the degree of ionization increases, as can be seen in Fig. 8. This behavior is expected from LeChatelier's law.

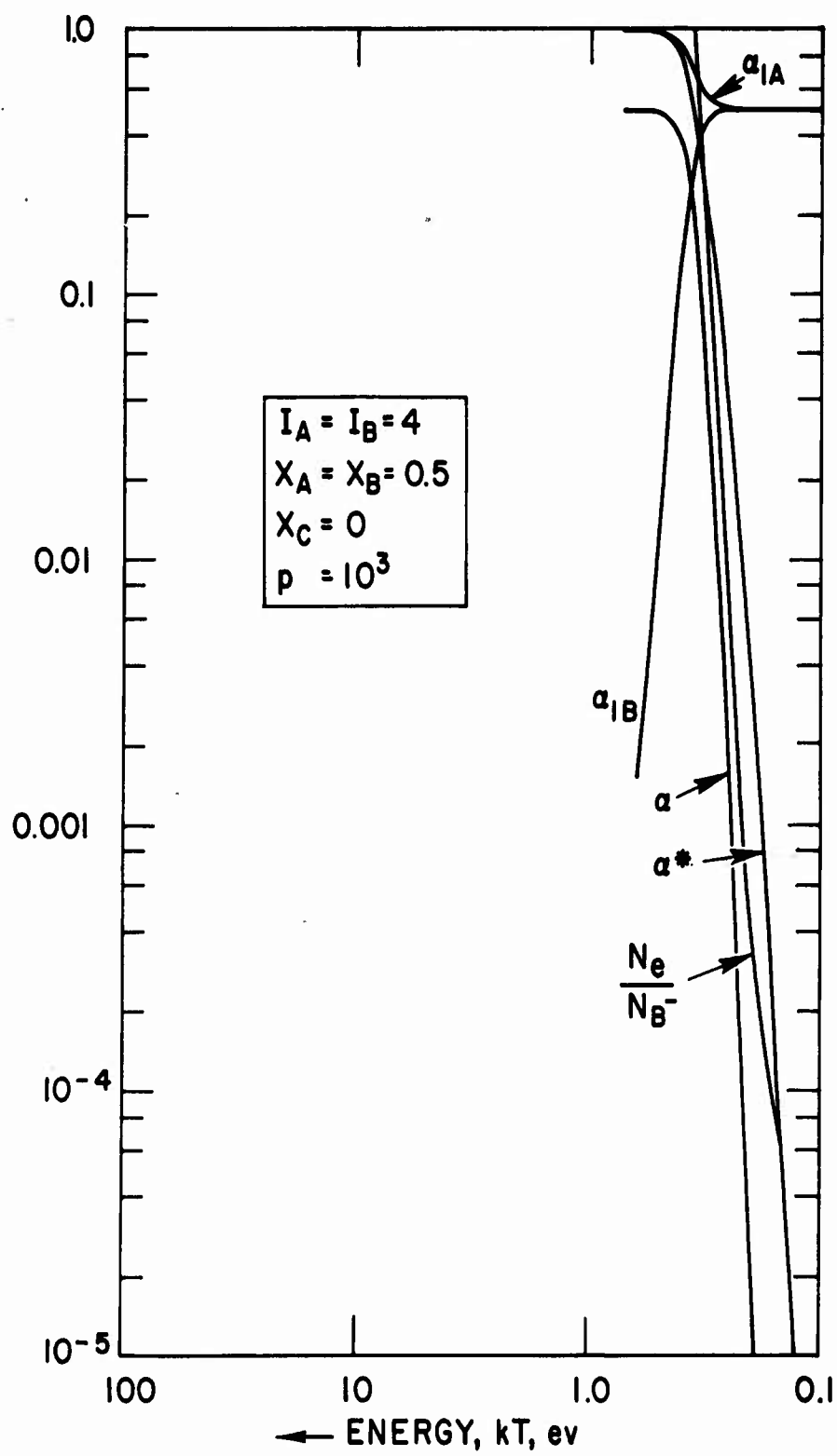


Fig. 7. Degree of ionization for a (4, 4) mixture with equal amounts of A and B.

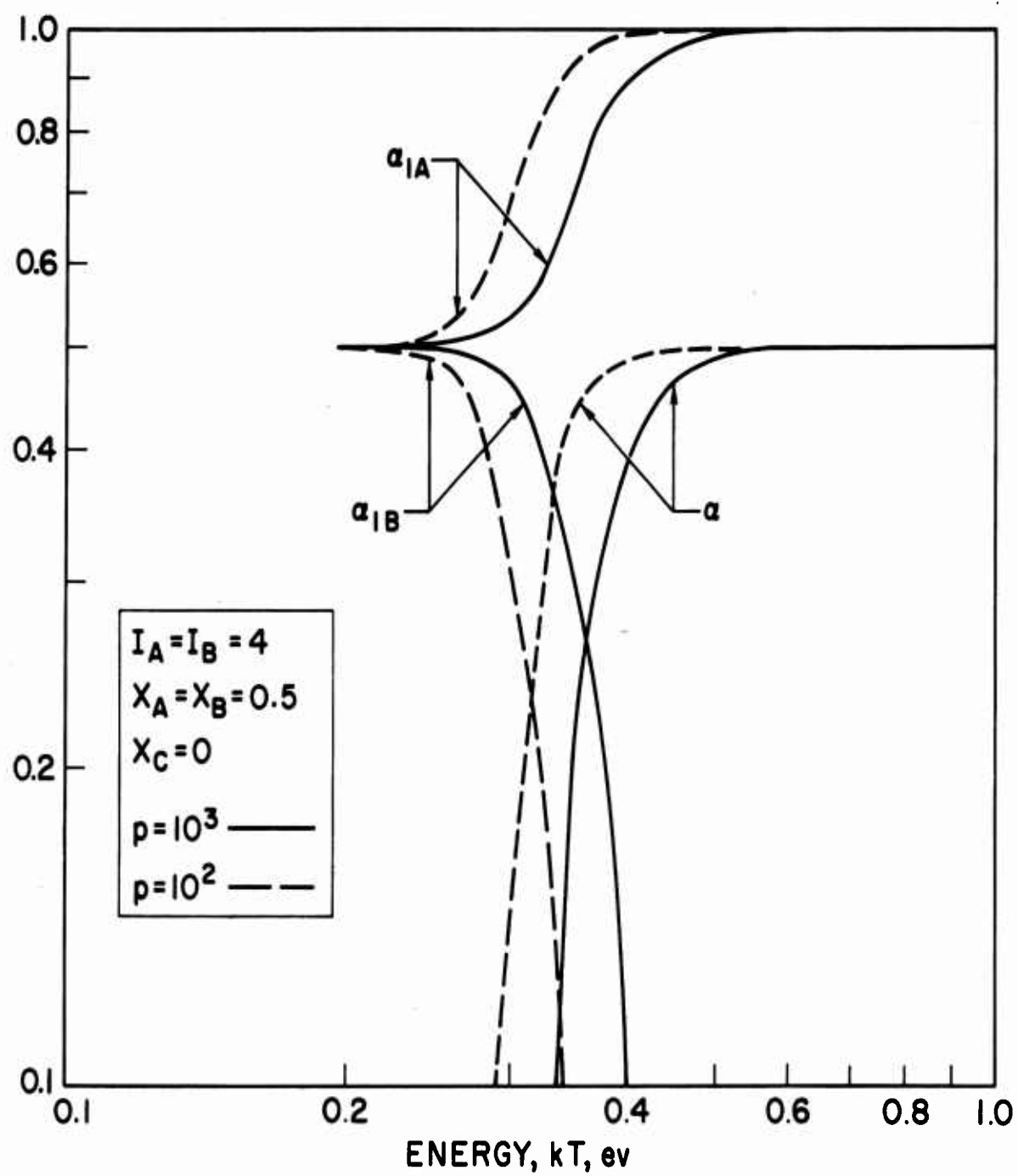


Fig. 8. Influence of pressure on degree of ionization of a (4, 4) mixture with equal amounts of A and B.

Two species which have the required characteristics of $I_A = I_B$ (nearly) are Group I and Group VII elements. The values are shown in the following table.

| <u>Group I Element</u> | <u>Ionization Potential, ev</u> | <u>Group VII Element</u> | <u>Electron Affinity, ev</u> |
|----------------------------|-------------------------------------|------------------------------|----------------------------------|
| Li | 5.4 | F | 4.1 |
| Na | 5.1 | Cl | 3.8 |
| K | 4.3 | Br | 3.6 |
| Rb | 4.2 | I | 3.2 |
| Cs | 3.9 | | |

Unfortunately, these species combine with a diatomic bond energy comparable to the ionization potential. To obtain an all-ion plasma, it is necessary to find molecules with $I_A \approx I_B$ and with A - B bond energy less than I_A .

SECTION IV

THREE-SPECIES GAS MIXTURES

The gas mixtures discussed in this section are composed of three different molecules: A, B, and C. A and C ionize to form positive ions; molecule B forms a negative ion B^- . Only trace amounts of B and C are added to A. The gas mixture is identified by the ionization potentials and electron affinities written as (I_A, I_B, I_C) . Hence, a (16, 2, 4) mixture has trace amounts of moderately electronegative and easily ionized species in a gas with high ionization potential. Three mixtures are studied: (16, 4, 4), (16, 2, 4), and (16, 4, 2).

For a three-species mixture, the formula for α is

$$\frac{\alpha}{1+\alpha} = \frac{X_A}{1+\alpha\left(1+\frac{p}{K_A}\right)} + \frac{X_B}{1+\alpha\left(1+\frac{p}{K_B}\right)} - \frac{X_B}{1+\alpha} + \frac{X_C}{1+\alpha\left(1+\frac{p}{K_C}\right)} \quad (20)$$

The formula for degree of ionization of C is the same as Eq. (9) with A replaced by C.

A. (16, 4, 4) Mixture

Three sets of graphs appear in Figs. 9, 10, and 11. For all of the graphs, $p = 10^4$ newtons/m² and $X_B = 0.01$. The amount of C is increased from graph to graph with values of 0.001, 0.01, and 0.02.

It is useful to introduce a quantity α^{**} , the ionization for a gas mixture of A and C. The influence of the electronegative B can be seen by comparing α and α^{**} . At low energy, α_{1B} approaches $X_C/(X_B + X_C)$. As temperature increases, α_{1B} decreases rapidly. At low energy, α_{1C} approaches $X_B/(X_B + X_C)$; and as energy of gas increases, α_{1C} approaches unity. These limits are readily apparent in Figs. 9, 10, and 11.

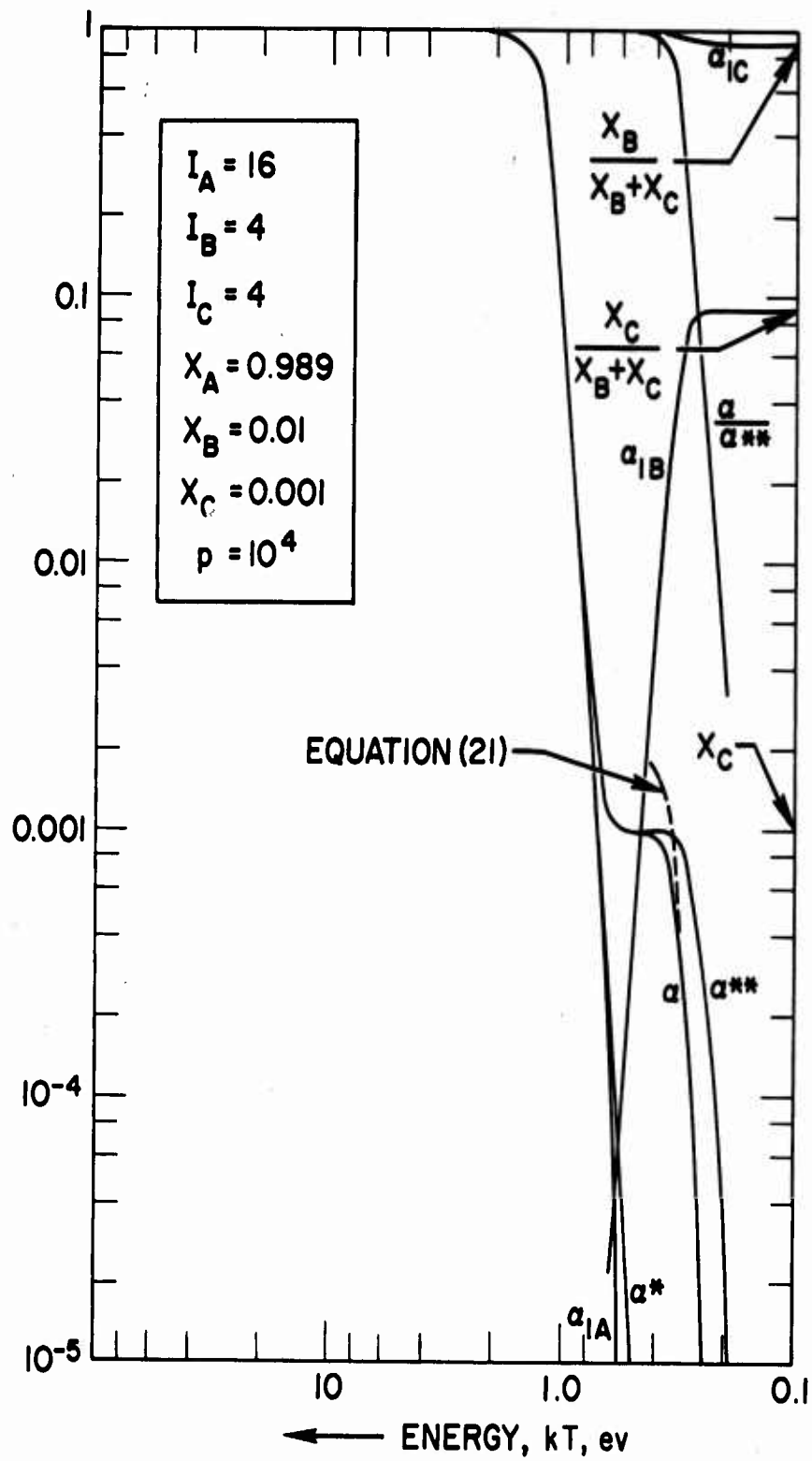


Fig. 9. Degree of ionization for (16, 4, 4) mixture with $X_C = 0.001$.

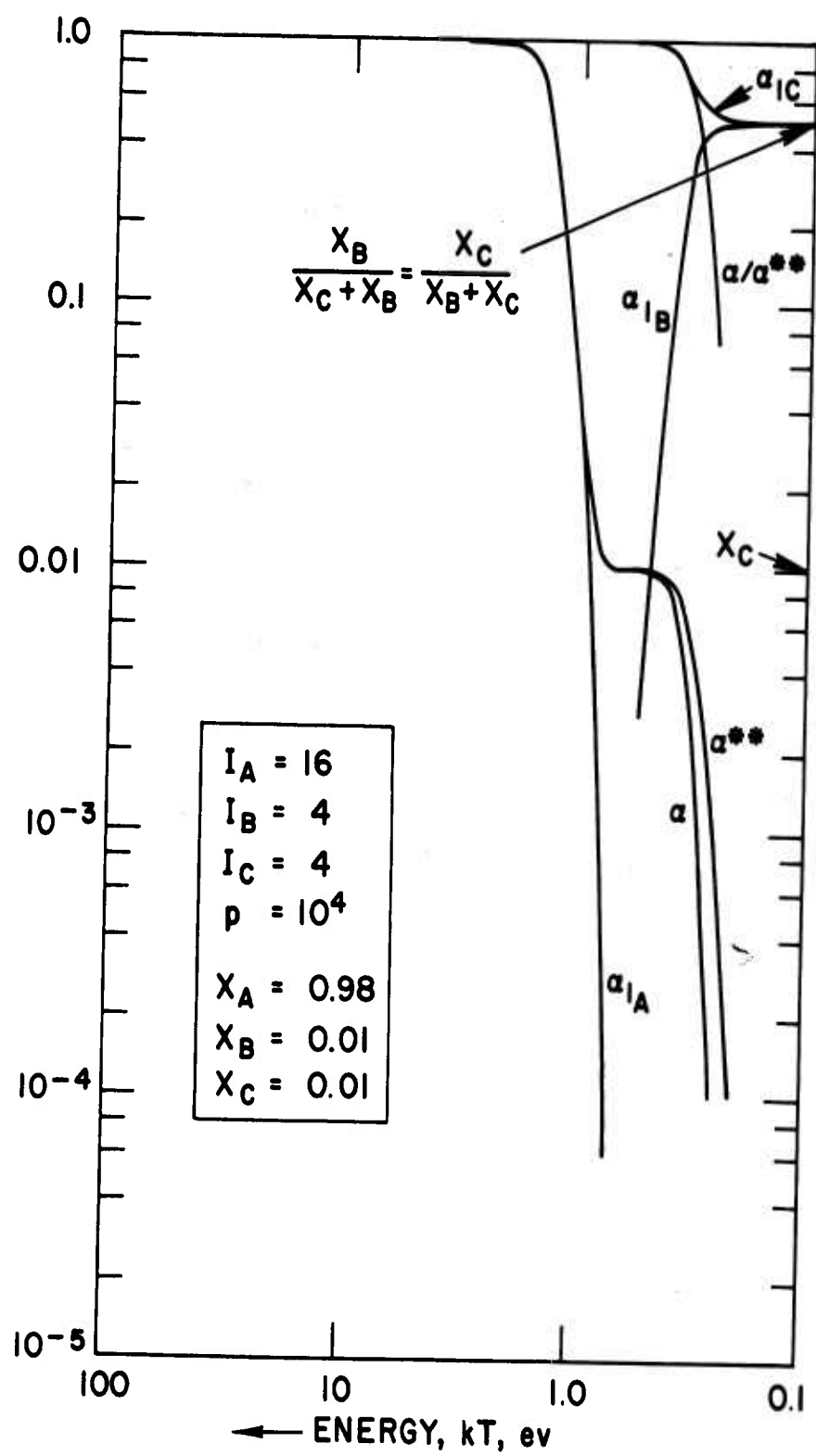


Fig. 10. Degree of ionization for (16, 4, 4) mixture with $X_C = 0.01$.

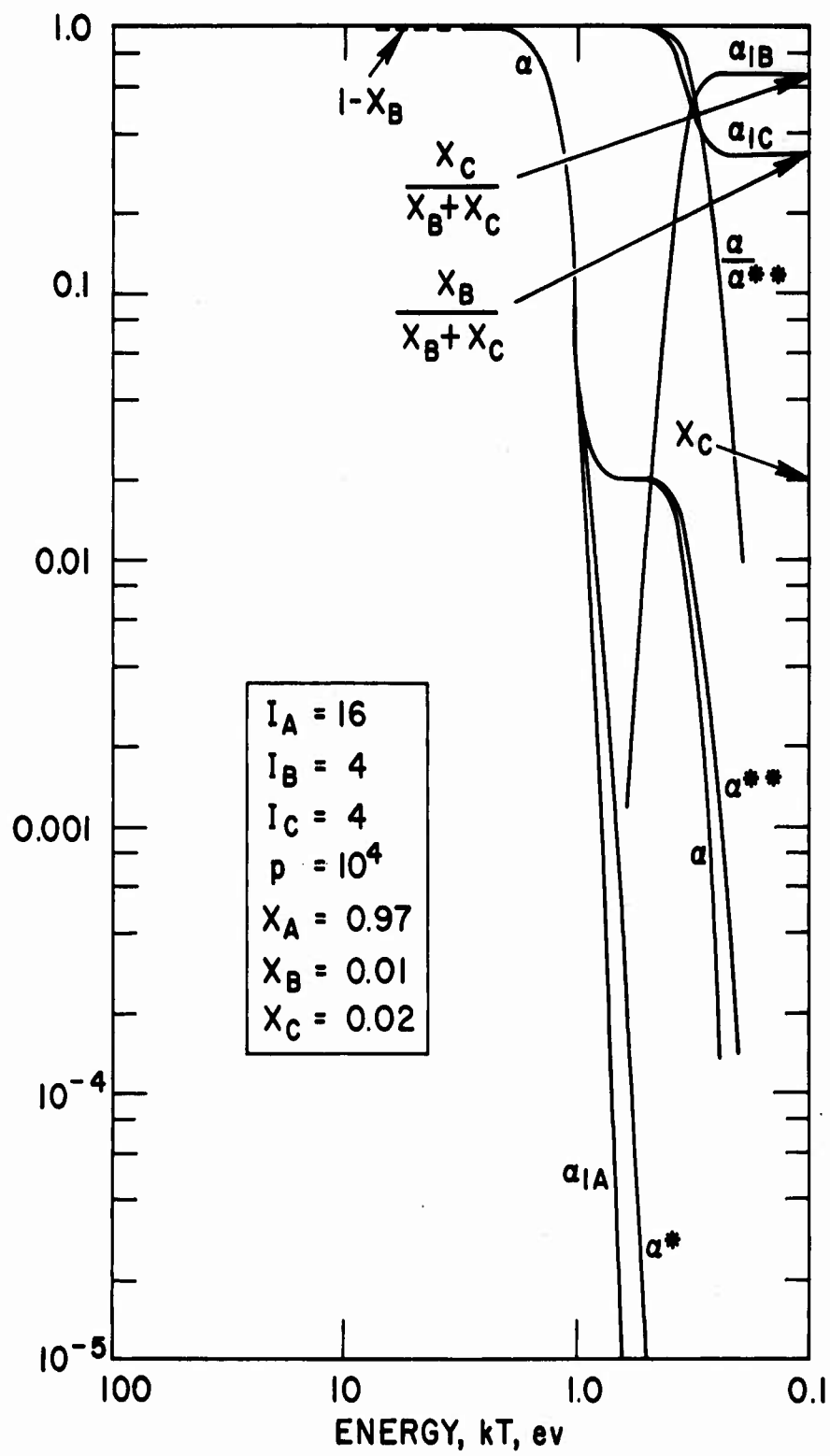


Fig. 11. Degree of ionization for (16, 4, 4) mixture with $X_C = 0.02$.

There is a step in α at a value $\alpha = X_C$. This is due to the fact that C is completely ionized while A has not been appreciably ionized. The energy for the step is about $I_C/10$. At an energy of $I_A/10$, α is approaching its high-energy asymptotic value of $1 - X_B$.

For low energy, it is possible to solve explicitly for α by neglecting the ionization of A. The equation is

$$\alpha = \frac{X_A + X_B K}{2K} \left[\sqrt{1 + \frac{4X_C K}{(X_A + X_B K)^2}} - 1 \right] \quad (21)$$

The subscript has been omitted in Eq. (21); K is equal to K_B or K_C . Since Eq. (21) does not depend on K_A , the gas mixture behaves as if A were inert at low energy. Equation (21) is plotted in Fig. 9.

Figure 9 can be compared with Fig. 5. At low energy, A and B of Fig. 5 behave the same as B and C of Fig. 9. Figure 5 is for $p = 10^3$ and $X_B = 0.1$, and Fig. 9 is for $p = 10^4$ and $X_B = 0.01$. In Fig. 5, α_{1B} starts to fall from its asymptotic value at about $kT = 0.3$; likewise α_{1B} for (16, 4, 4) mixture starts to fall at $kT = 0.3$. The gas mixture ABC behaves at low energy as if A were inert.

At high temperature, a (16, 4, 4) mixture behaves like the (16, 4) mixture shown in Fig. 2.

B. (16, 2, 4) Mixture

This mixture has trace amounts ($X_B = X_C = 0.01$) of a moderately electronegative (electron affinity of 2 ev) and is easily ionized (ionization potential 4 ev) in a gas with high ionization potential (16 ev). The results of the calculations are presented graphically in Fig. 12.

Due to the energy separation of I_A and I_C , species C ionizes first giving the step from $kT = 0.4$ to 0.6 ev. The presence of B does not cause

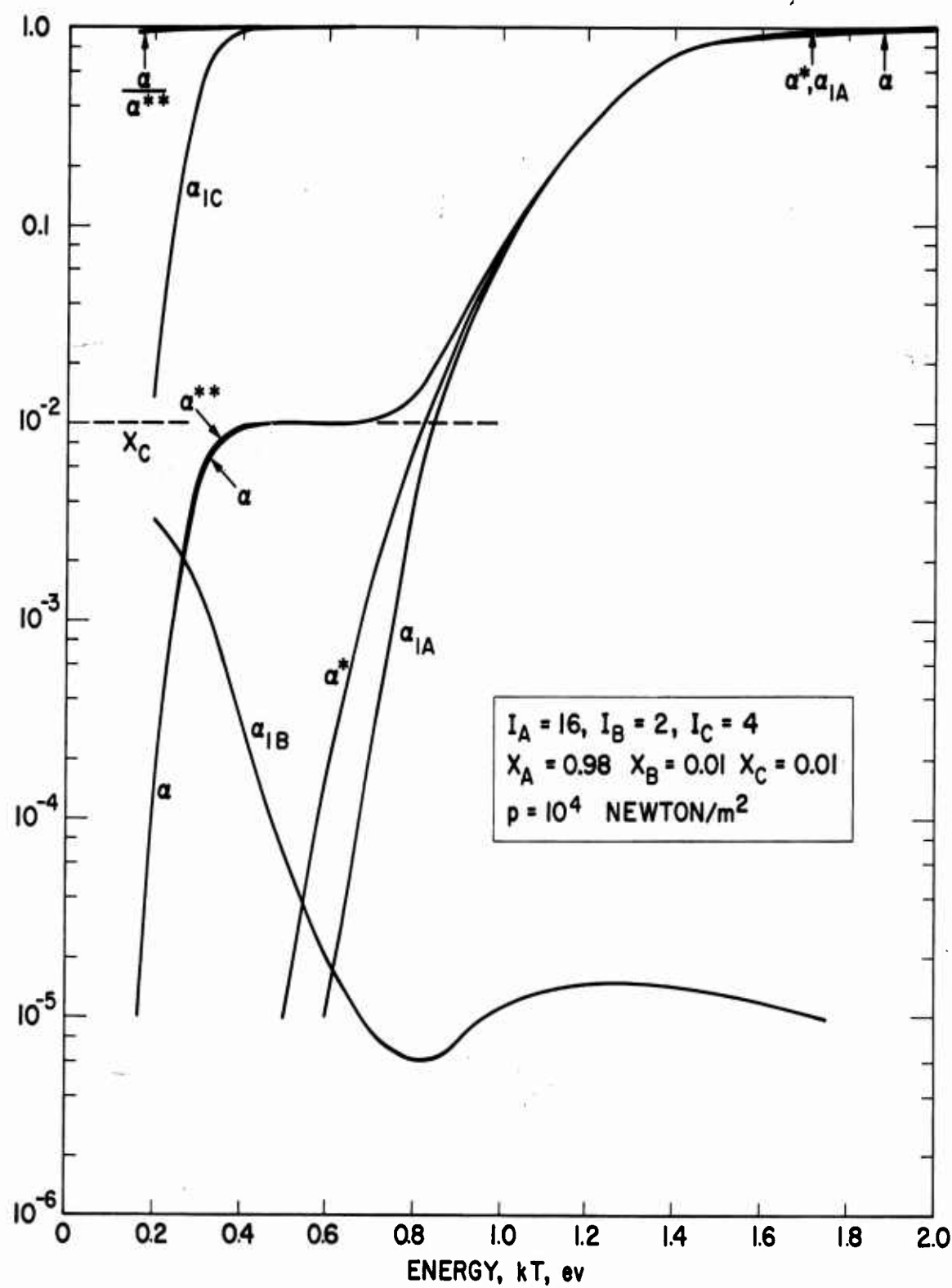


Fig. 12. Degree of ionization for (16, 2, 4) mixture.

significant changes; α^{**} is almost indistinguishable from α . The maximum number of negative ions formed is only about 3 out of every 1000 B molecules. The fraction of B ionized decreases, going through a minimum at about 0.82 ev. When the available electrons increase due to ionization of A, α_{1B} increases reaching a maximum at about 1.3 ev. In the interval of kT from 0.2 to 0.6 ev, the behavior of B and C is qualitatively the same as A and B in Fig. 3. Above 0.6 ev up to 2.0 ev, C is fully ionized and A and B behave the same as do A and B in Fig. 2. Figure 12 is qualitatively the composite graph of Figs. 3 and 4 spliced together at about 0.6 ev.

C. (16, 4, 2) Mixture

Calculations were performed for $X_B = X_C = 0.01$ and $p = 10^4$ newtons/m², the same values as for the (16, 2, 4) mixture. One might expect α and α_{1A} to show different trends for a (16, 4, 2) mixture. However, comparison of Figs. 12 and 13 shows that the curves are identical! When $X_B = X_C$, and when I_B and I_C magnitudes are interchanged, the values of α and α_{1A} remain the same. These results for this special case can be verified by considering the last three terms in Eq. (21).

At low energy, nearly all the B and C molecules are ionized. The reason that α remains the same for (16, 4, 2) mixture as for (16, 2, 4) mixture is that the numerous extra electrons produced due to C^+ are removed by B in the form of B^- . It is interesting to note that $X_B = X_C$, if the origin of B and C were dissociation of a diatomic molecule BC.

The ratio of electron density in the "deseeded" mixture to the electron density in the seeded mixture, α/α^{**} , is plotted in both Figs. 12 and 13. As would be expected from the study of the (2, 4) mixture, the electronegative species has little influence on the (16, 2, 4) mixture. However, the presence of B in the (16, 4, 2) mixture has a pronounced influence up to a temperature corresponding to $kT = 0.25$. At $kT = 0.18$, the mixture is deseeded by a factor 10^{-3} .

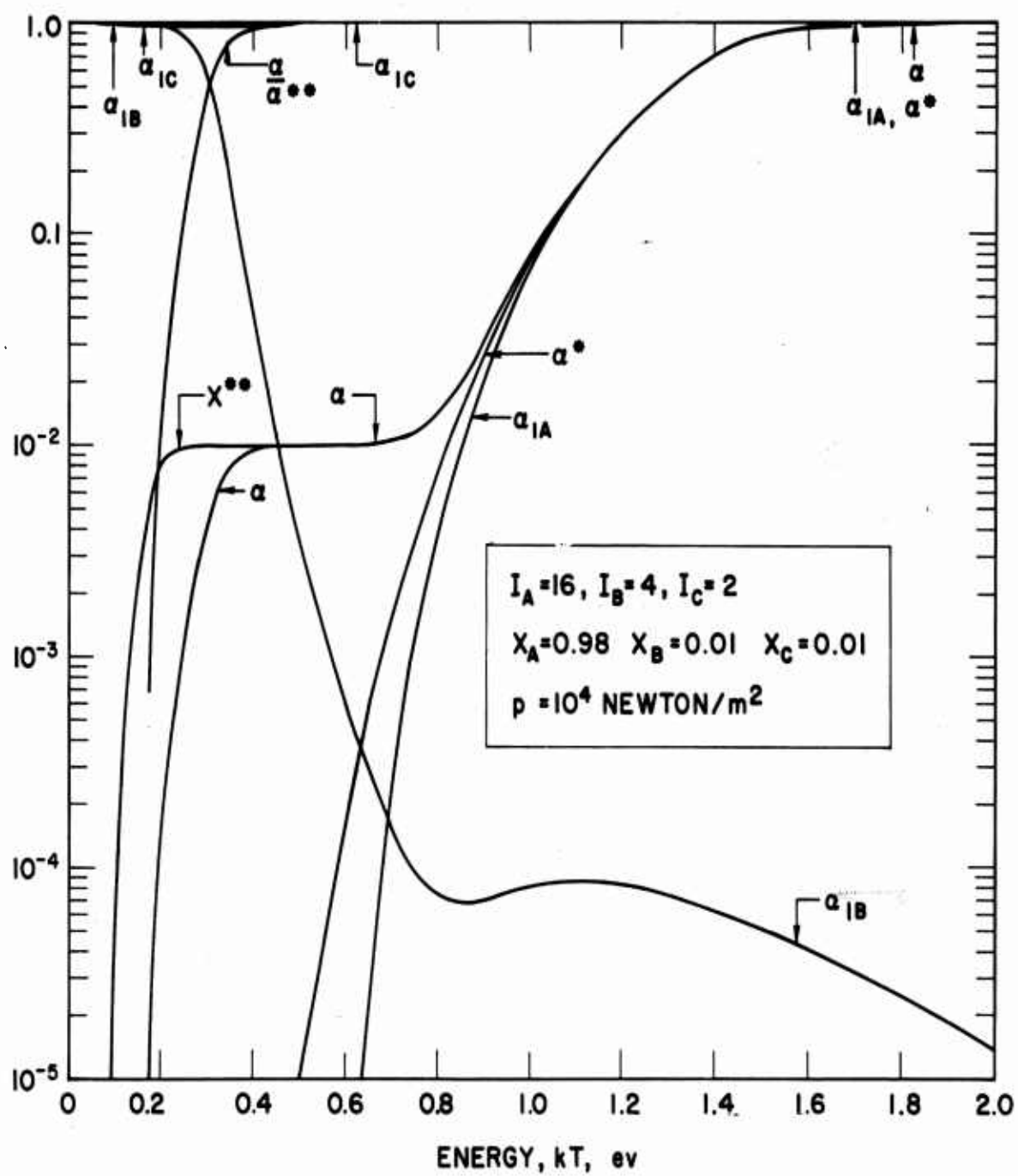


Fig. 13. Degree of ionization for (16, 4, 2) mixture.

SECTION V

ADDITION OF SF₆ TO AN ARGON PLASMA JET

Various amounts of SF₆ were mixed in the plenum chamber of the arc jet as shown in Fig. 14. Power to the arc, argon mass flow and plenum chamber and exit pressures were maintained constant. The electrical conductivity was monitored using the meter described in Ref. 6. The experimental results and the theoretical curve are shown in Fig. 14. The decrease in conductivity is due to two causes: cooling and removal of electrons by electronegative species.

$$\frac{\sigma}{\sigma_0^*} = \left(\begin{array}{c} \text{cooling} \\ \text{effect} \end{array} \right) \left(\begin{array}{c} \text{electronegative} \\ \text{removal of electrons} \end{array} \right) = \frac{\sigma^*}{\sigma_0^*} \frac{\sigma}{\sigma^*}, \quad (22)$$

where σ = conductivity at kT and with SF₆ addition

σ^* = conductivity at kT of pure argon jet

σ_0^* = conductivity at kT_0 of pure argon jet

For small changes in kT , σ^*/σ_0^* was calculated using the slope of α^* versus kT as shown in Fig. 2. (The region near static temperature of 0.77 ev was replotted using expanded linear coordinates.) It was assumed that σ is proportional to α . Hence,

$$\frac{\sigma^*}{\sigma_0^*} = 1 + \frac{\partial(\alpha^*/\alpha_0^*)}{\partial kT} (kT - kT_0) \quad (23)$$

When $(kT - kT_0)$ exceeded 0.2 ev, α^*/α_0^* was taken from Fig. 2. The kT with added SF₆ was calculated by reducing the stagnation enthalpy of argon component by an amount $X_{\text{SF}_6} C_p T$. T is stagnation temperature and

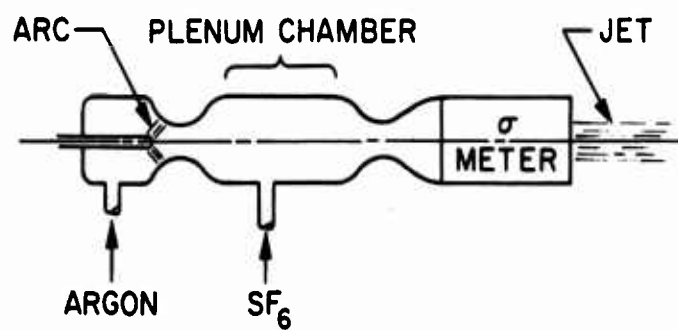
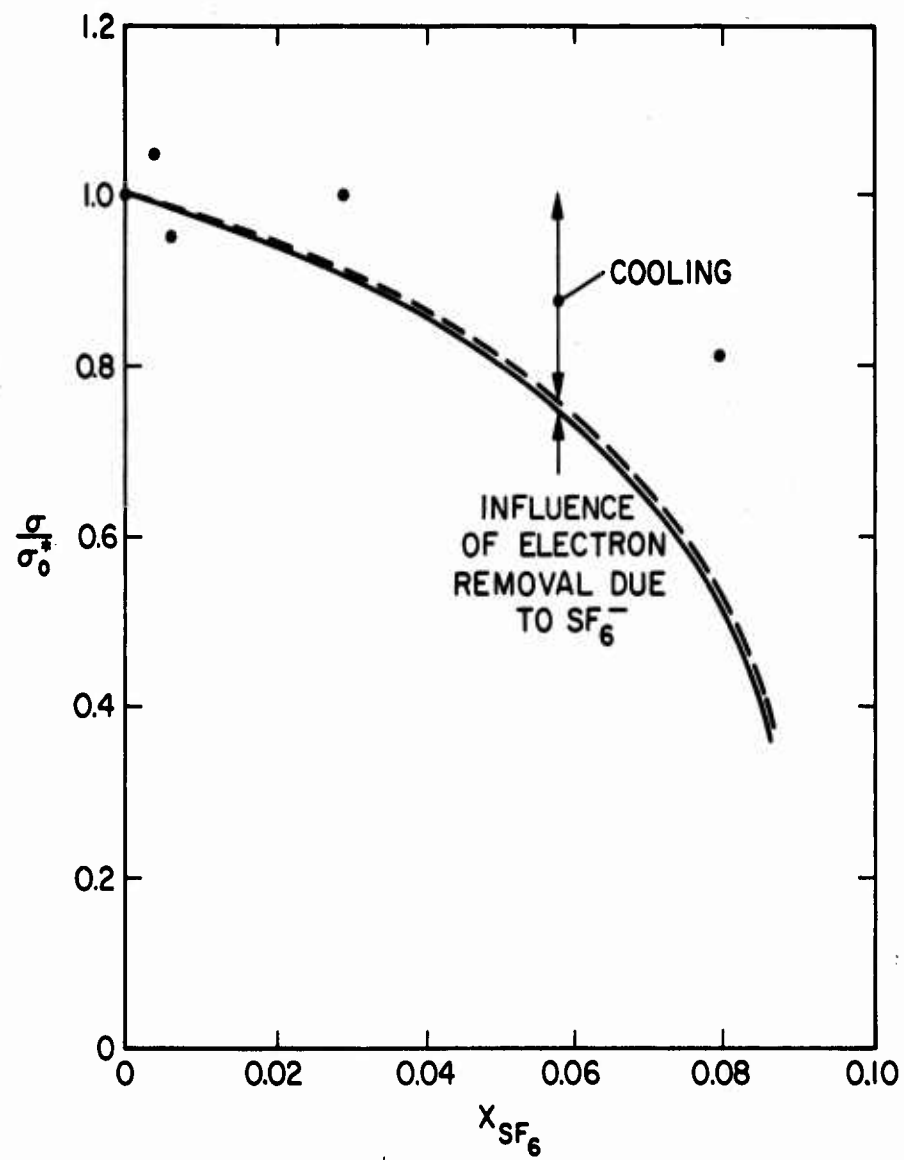


Fig. 14. Comparison of experimental results with theoretical prediction for the argon- SF_6 experiment.

$C_p = 19R$ is specific heat at constant pressure. The gas mixture was assumed to expand isentropically from plenum chamber to exit pressure.

Reference to Fig. 2 shows that for the temperature interval $0.70 < kT < 0.77$, α/α^* is equal to $X_{Ar}^{1/2}$. The influence of SF_6 is

$$\frac{\sigma}{\sigma^*} = X_{Ar}^{1/2} \quad (24)$$

The curve shown in Fig. 14 was calculated using the product of Eqs. (23) and (24). The decrease in conductivity is due mainly to cooling of the gas. Experimental results are consistent with a crude estimate of the decreased conductivity.

A more definitive test would be to conduct an experiment in which $I_A \cong I_B$. As discussed previously, this should give significant electron removal.

SECTION VI

CONCLUSIONS

The influence of an electronegative species on thermal ionization in a two-species mixture of gases depends on the ratio of electron affinity to ionization potential. When this ratio is greater than unity, the electron density is decreased effectively up to $kT \cong I_A/20$. When the ratio is unity, the result is similar; i. e., electrons are effectively removed up to $kT \cong I_A/20$ to $I_A/10$. When the ratio is less than unity, only a very small fraction [2×10^{-5} for (16, 4) mixture and 3×10^{-2} for (4, 2) mixture] of the B form B^- .

Trace amounts of an electronegative (B) and an easily ionized species (C) added to a gas with relatively large ionization potential (A) gives the same results, at low energy, as described in the preceding paragraph. At low energy, A behaves as an inert gas, and it is the ratio of I_B/I_C that determines the amount of electron removal or deseeding.

Electronegative molecules do not significantly "soak up" electrons above about $I/10$. The largest observed electron affinity is about 4 ev. It is not feasible to try to remove electrons by forming negative ions above about 4500°K when thermodynamic equilibrium prevails.

A gas mixture having one species with electron affinity comparable to the ionization potential of another species forms an all-ion plasma at low temperature.

Experimentally, the decrease in conductivity of an argon arc plasma jet with a trace amount of SF_6 added is consistent with theoretical predictions.

ACKNOWLEDGEMENTS

The author is grateful for helpful discussions with D. M. Dix and R. Betchov.

Adam Klizewski programmed Eq. (20) for the computer. His contribution has been invaluable.

O. L. Gibb assisted with the argon-SF₆ experiment.

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APPENDIX

TABLES OF $K(I, kT)$

Equation (4) has been calculated for kT for $I = 0, 1, 2, 4, 16$. The results are tabulated in this appendix. The ratio of partition functions is unity.

$K(0, kT)$ is equal to

$$\left(\frac{2\pi m_e}{h^2}\right)^{3/2} (kT)^{5/2}, \quad (A1)$$

and has been included to show the influence of this quantity on K . Also, $K(I, kT) = K(0, kT) \exp(-I/kT)$.

Further, it is possible to calculate K for any value of I by using the tabulated values of $K(1, kT)$ and the relation

$$K(I, kT) = I^{5/2} K\left(\frac{kT}{I}\right) = I^{5/2} K\left(1, \frac{kT}{I}\right) \quad (A2)$$

A numerical example is

$$K(16, 8) = (16)^{5/2} K\left(1, \frac{8}{16}\right)$$

or

$$0.1185 \times 10^{11} = (1024)(0.1157 \times 10^8)$$

TABLE OF K(I, KT)

| KT | I = 0 | I = 1 | I = 2 | I = 4 | I = 16 |
|------------|------------|------------|------------|------------|------------|
| 0.1000E-00 | 0.1530E 07 | 0.6945E 02 | 0.3153E-02 | 0.6499E-11 | 0. |
| 0.1200E-00 | 0.2413E 07 | 0.5800E 03 | 0.1394E-00 | 0.8056E-08 | 0. |
| 0.1400E-00 | 0.3548E 07 | 0.2804E 04 | 0.2217E 01 | 0.1385E-05 | 0. |
| 0.1600E-00 | 0.4954E 07 | 0.9563E 04 | 0.1846E 02 | 0.6880E-04 | 0. |
| 0.1800E-00 | 0.6650E 07 | 0.2571E 05 | 0.9938E 02 | 0.1485E-02 | 0. |
| 0.2000E-00 | 0.8654E 07 | 0.5831E 05 | 0.3929E 03 | 0.1784E-01 | 0.1562E-27 |
| 0.2500E-00 | 0.1512E 08 | 0.2769E 06 | 0.5071E 04 | 0.1701E 01 | 0.2425E-20 |
| 0.3000E-00 | 0.2385E 08 | 0.8507E 06 | 0.3035E 05 | 0.3862E 02 | 0.1641E-15 |
| 0.3500E-00 | 0.3506E 08 | 0.2014E 07 | 0.1156E 06 | 0.3814E 03 | 0.4913E-12 |
| 0.4000E-00 | 0.4895E 08 | 0.4018E 07 | 0.3298E 06 | 0.2222E 04 | 0.2080E-09 |
| 0.5000E+00 | 0.8552E 08 | 0.1157E 08 | 0.1566E 07 | 0.2869E 05 | 0.1083E-05 |
| 0.6000E 00 | 0.1349E 09 | 0.2548E 08 | 0.4812E 07 | 0.1717E 06 | 0.3539E-03 |
| 0.7000E 00 | 0.1983E 09 | 0.4753E 08 | 0.1139E 08 | 0.6542E 06 | 0.2348E-01 |
| 0.8000E 00 | 0.2769E 09 | 0.7934E 08 | 0.2273E 08 | 0.1866E 07 | 0.5708E 00 |
| 0.9000E 00 | 0.3717E 09 | 0.1224E 09 | 0.4028E 08 | 0.4366E 07 | 0.7070E 01 |
| 0.1000E 01 | 0.4838E 09 | 0.1780E 09 | 0.6547E 08 | 0.8860E 07 | 0.5444E 02 |
| 0.1500E 01 | 0.1333E 10 | 0.6844E 09 | 0.3514E 09 | 0.9263E 08 | 0.3107E 05 |
| 0.2000E 01 | 0.2737E 10 | 0.1660E 10 | 0.1007E 10 | 0.3704E 09 | 0.9180E 06 |
| 0.3000E 01 | 0.7541E 10 | 0.5403E 10 | 0.3872E 10 | 0.1988E 10 | 0.3641E 08 |
| 0.4000E 01 | 0.1548E 11 | 0.1206E 11 | 0.9389E 10 | 0.5695E 10 | 0.2835E 09 |
| 0.5000E 01 | 0.2704E 11 | 0.2214E 11 | 0.1813E 11 | 0.1215E 11 | 0.1102E 10 |
| 0.7000E 01 | 0.6272E 11 | 0.5437E 11 | 0.4713E 11 | 0.3542E 11 | 0.6378E 10 |
| 0.8000E 01 | 0.8757E 11 | 0.7728E 11 | 0.6820E 11 | 0.5311E 11 | 0.1185E 11 |
| 0.1000E 02 | 0.1530E 12 | 0.1384E 12 | 0.1252E 12 | 0.1025E 12 | 0.3089E 11 |

Note: E09 is 10⁹.

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